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Towards the upgrading of fermentation broths to advanced biofuels: a water tolerant catalyst for the conversion of ethanol to isobutanol†

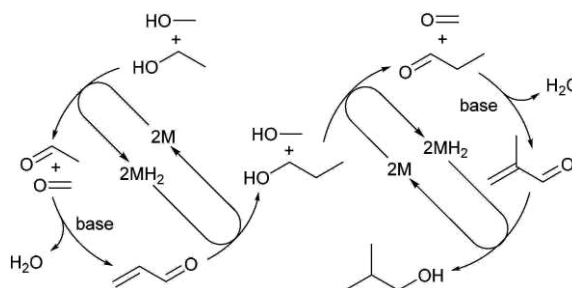
Katy J. Pellow,  Richard L. Wingad  and Duncan F. Wass  *

Isobutanol is an ideal gasoline replacement due to its high energy density, suitable octane number and compatibility with current engine technology. It can be formed by the Guerbet reaction in which (bio)ethanol and methanol mixtures are converted to this higher alcohol in the presence of a suitable catalyst under basic conditions. A possible limitation of this process is the catalyst's water tolerance; a twofold problem given that water is produced as a by-product of the Guerbet reaction but also due to the need to use anhydrous alcoholic feedstocks, which contributes significantly to the cost of advanced biofuel production. Isobutanol formation with pre-catalyst $\text{trans}[\text{RuCl}_2\text{I}(\text{dppe})_2]$ (1) has been shown to be tolerant to the addition of water to the system, achieving an isobutanol yield of 36% at 78% selectivity with water concentrations typical of that of a crude fermentation broth. Key to this success is both the catalyst's tolerance to water itself and the use of a hydroxide rather than an alkoxide base; other catalysts explored are less effective with hydroxides. Alcoholic drinks have also been used as surrogates for the fermentation broth: the use of lager as the ethanol source yielded 29% isobutanol at 85% selectivity in the liquid phase.

Introduction

The need to find sustainable alternatives to liquid fossil fuels for transportation is crucial both from an environmental perspective and to ensure energy security for the future.¹ The most widely used alternative to gasoline is bioethanol, derived from the fermentation of biomass.² But bioethanol is by no means an ideal gasoline replacement; it is corrosive to engine technology, has a significantly lower energy density than gasoline and its hygroscopic nature leads to storage problems.³ By contrast, butanols have fuel characteristics much closer to those of conventional gasoline and are often considered 'advanced biofuels' because of their superior performance.⁴ Biosustainable routes to butanol, such as the ABE (acetone–butanol–ethanol) process, remain challenging.⁵ Our group has investigated converting readily available (bio)ethanol to n-butanol using homogeneous ruthenium catalysts with either P–P bidentate or mixed donor P–N ligands, achieving excellent selectivity at good conversion for this transformation.⁶ There have been several other recent examples of the conversion of ethanol to n-butanol using homogeneous ruthenium or iridium catalysts which demonstrate similar performance.⁷ This area and related heterogeneous approaches have been extensively reviewed over the last few years.⁸

We recently reported that our family of ruthenium catalysts are also capable of converting ethanol/methanol mixtures to isobutanol with high ethanol conversions to Guerbet alcohol products (>75%) and excellent selectivity for isobutanol formation (>99%), the first homogeneous catalysts for this reaction.⁹ Heterogeneous systems have been known since 1990 (ref. 10) and very recently a homogeneous ruthenium(I,II) bis(phosphino–phosphinine) pre-catalyst has been reported.¹¹ Our interest in forming isobutanol lies in the fact that it offers improved fuel properties over n-butanol, such as a higher octane number and energy density (98% of that of gasoline).¹² A Guerbet-type mechanism was proposed (Scheme 1) for the formation of isobutanol; this "borrowed hydrogen" process requires two cycles (ethanol/methanol to propanol and propanol/methanol to isobutanol) and



Scheme 1 Co-condensation of ethanol and methanol via Guerbet chemistry.

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† Electronic supplementary information (ESI) available: Experimental details and NMR spectra.

consequently two equivalents of water are produced as the only by-product. Clearly, it is important that Guerbet catalysts demonstrate good water tolerance so as not to be poisoned by this by-product. Another important consideration in terms of sustainable technology is the recovery of 'dry' bioethanol from a typical fermentation broth (Fig. 1). This is achieved by distillation, yielding typically 95.6 wt% ethanol when corn starch is used.¹³ Molecular sieves are then used in the final drying process to yield >99% pure ethanol. This is a highly energy intensive process; in fact, during the production of first generation bioethanol, typically over half of the energy is consumed in the drying procedures.^{7b} It is clear that using a fermentation broth rather than analytically pure ethanol as a substrate in ethanol-to-butanol catalysis would be highly desirable (Fig. 1, ideal pathway), and could significantly impact the economics and sustainability of such a process. Removing the need to dry ethanol before upgrading to butanol means that only one drying step is required in which the water from the fermentation broth and that formed during the Guerbet cycle can be removed in a single purification step. Water/isobutanol separation by distillation is also much easier to achieve than ethanol/water distillation. Even using approximately 95 wt% ethanol could lead to benefits in this regard (Fig. 1, alternative pathway). Unfortunately, many Guerbet catalytic systems are reported to lose activity and selectivity in the presence of water.^{6c,7e,14} Water can potentially lead to catalyst decomposition or solubility issues, and deactivation of alkoxide bases to often inactive hydroxides.^{10b,15} Water may also promote the formation of carboxylate salts and esters in competing reactions, lowering the product selectivity and the basicity of the reaction mixture.^{7d,14b,16} Indeed a recent review by Wang and Cao highlights that the vast majority of bioethanol upgrading systems utilise anhydrous feedstocks, with attempts to use "wet" ethanol showing only limited success.¹⁷ Xu and Mu et al. have developed immobilised iridium catalysts capable of converting either ethanol to n-butanol or mixtures of ethanol and methanol to isobutanol under aqueous conditions with

impressive yields and selectivity; however, the system is limited by the long reaction times that are needed to ensure high ethanol conversion.^{7b,10d}

In our preliminary communication on homogeneous methanol/ethanol to isobutanol catalysts,⁹ we focused on our standard catalyst screening conditions (using analytically pure methanol/ethanol) without studying these systems with more realistic alcohol/water mixtures and probing the all-important effect of water levels and base selection and concentration. We now report in detail the effect of these parameters with several ruthenium based catalysts, showing that surprisingly good conversions can still be achieved with trans-[RuCl₂(Jdppm)]₂ (1) at high levels of water. In addition, experiments with alcoholic beverages, used as surrogates for fermentation broths, reveal that 1 can also tolerate biogenic impurities.

Results and discussion

Catalyst screening

We have previously reported the use of ruthenium pre-catalysts 1 and 2, which utilise P–P or P–N bidentate ligands, to upgrade ethanol/methanol mixtures to isobutanol in high yield and excellent selectivity (Table 1, entries 1 and 9).⁹ In this paper we have investigated the impact of using wet ethanol/methanol mixtures on these two catalysts and also pre-catalyst 3, which possesses a P–N–P tridentate ligand. Complex 3 is a commercially available hydrogenation/dehydrogenation pre-catalyst which shows excellent activity in related alcohol conversions and therefore we felt that it may perform well in our system.¹⁸ We employed our standard reaction conditions of sodium methoxide base, a methanol to ethanol molar ratio of 14.4 : 1 (to prevent homocoupling of ethanol), a catalyst loading of 0.1 mol% (relative to ethanol) and a reaction temperature of 180 °C. The performance of catalyst 3 is comparable to that of catalyst 2 after two hours (entry 12).[‡] An increase in reaction time led to a modest increase in both yield and selectivity for isobutanol formation (entry 13). Accompanying the formation of liquid Guerbet products using pre-catalysts 1–3 was the formation of solid products, sodium formate, carbonate and acetate, and associated significant hydrogen evolution. The origin of these products will be discussed in the following section.

Base investigation

With a selection of catalysts in hand, we first considered the choice of base before attempting to add water to the system. Addition of water to the reaction mixture results in the conversion of sodium methoxide base to methanol and sodium hydroxide. In our previous communication, we reported that a combination of 1 and co-catalyst sodium hydroxide was able to efficiently convert ethanol/methanol mixtures to isobutanol⁹

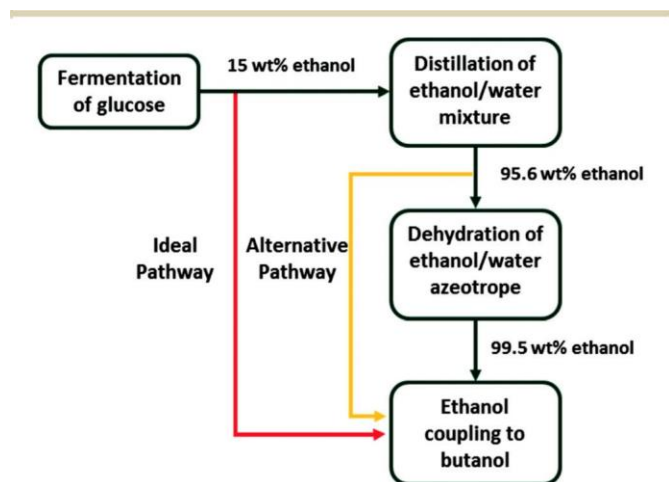


Fig. 1 The drying stages involved in obtaining anhydrous ethanol for catalytic upgrading.

[‡] 2 h was chosen as the standard reaction time as the production of isobutanol significantly slowed after this time in the kinetic experiments with complex 1 (see the ESI,[†] section 3).

Table 1 Conversion of ethanol/methanol to isobutanol

$\text{CH}_3\text{CH}_2\text{OH} + 2 \text{CH}_3\text{OH} \xrightarrow[180^\circ\text{C, 2-20 h}]{0.1 \text{ mol\% [Ru], 50-200 mol\% base}} \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + 2 \text{H}_2\text{O}$							
Entry ^a	Catalyst	Base (mol%)	Added water (mL)	Ethanol conversion ^b (%)	Yield (selectivity) ^c (%)		
					Isobutanol	n-Propanol	Other
1 ^d	1	NaOMe (200)	—	67	65 (98)	1.2 (1.8)	0.8 (0.7)
2 ^d	1	NaOH (200)	—	74	71 (96)	2.8 (3.8)	0.5 (0.3)
3 ^d	1	NaOH (200)	0.62	74	71 (97)	2.2 (3.0)	0.4 (0.3)
4	1	NaOH (150)	—	75	72 (96)	2.4 (3.2)	0.8 (0.5)
5	1	NaOH (100)	—	67	59 (90)	5.3 (8.2)	2.6 (2.0)
6	1	NaOH (50)	—	17	11 (68)	3.9 (25)	2.4 (7.7)
7	1	NaOC(O)H (200)	—	0.2	0.1 (42)	0.1 (58)	—
8	1	Na ₂ CO ₃ (200)	—	0.2	0.1 (57)	0.1 (43)	—
9 ^d	2	NaOMe (200)	—	49	39 (86)	3.1 (6.8)	6.6 (7.2)
10	2	NaOH (200)	—	39	28 (74)	8.6 (23)	2.5 (3.3)
11	2	NaOH (200)	0.62	19	10 (55)	7.7 (41)	1.5 (3.9)
12	3	NaOMe (200)	—	48	36 (82)	4.7 (11)	7.1 (7.9)
13 ^e	3	NaOMe (200)	—	53	44 (89)	2.4 (4.8)	6.7 (6.7)
14	3	NaOH (200)	—	0.2	—	0.2 (100)	—
15	3	NaOH (200)	0.62	1.0	0.3 (48)	0.2 (20)	0.5 (32)

^a Conditions: 1 mL (17.13 mmol) ethanol, 10 mL (247.13 mmol) methanol, 0.1 mol% [Ru], base (mol% as stated) (mol% based on the ethanol substrate), 180 °C, 2 h. ^b Conversion of ethanol based on the total amount of liquid products obtained as determined by GC analysis. ^c Total yield and selectivity of Guerbet products in the liquid fraction as determined by GC analysis. ^d Previously reported by us.⁹ ^e 20 h.

even though hydroxide has proven to be detrimental in other Guerbet systems.^{10b,15} Given the high activity of 1 with hydroxide base, we felt that this warranted further investigation with other catalysts. Performing the catalysis with complex 2 and sodium hydroxide as the base did result in a decrease in both yield and selectivity compared to when sodium methoxide was the co-catalyst, however, a reasonable iso-butanol yield was still produced (Table 1, entry 10). Contrastingly, the use of sodium hydroxide as the base with catalyst 3 resulted in only a trace amount of propanol being formed in the liquid fraction as the sole Guerbet product (entry 14). As with the reaction with an alkoxide base, hydrogen was generated over the course of the reaction as evidenced by a pressure increase in the autoclave, concurrent with sodium formate, carbonate and acetate precipitation from the reaction mixture. § Beller et al. have previously reported that catalyst 3 in an open system readily converts ethanol to ethyl acetate, which, if formed in our system, may then be converted to sodium acetate and ethanol by sodium hydroxide.¹⁸ The same group have also demonstrated that methanol undergoes water/hydroxide assisted dehydrogenation to carbon dioxide (trapped as carbonate under basic conditions) using catalyst 3, with formate being observed as an intermediate.¹⁹ The use of a hydroxide base in our system presumably promotes similar processes, with the formation of these products being favoured over Guerbet coupling with pre-catalyst 3.

In comparison, the use of a hydroxide base with catalyst 1 actually led to a small increase in isobutanol yield compared to using sodium methoxide, and the high selectivity was maintained (entry 2).⁹ Significant levels of hydrogen, sodium carbonate and formate products were still produced over the course of the reaction but compared to catalyst 3 it appears that these processes do not dominate over Guerbet-type reactions. § Heating methanol only (to prevent Guerbet coupling), catalyst 1 and sodium hydroxide under our standard conditions resulted in the formation of significant residual pressure in the autoclave and the precipitation of sodium carbonate from the reaction mixture (see the ESI,† section 4.1). However, carrying out the same experiment with sodium methoxide instead of sodium hydroxide base did not result in precipitation of solids from the reaction mixture nor any observable residual pressure (see the ESI,† section 4.2). ¶ These results, in line with Beller's earlier work, demonstrate that water/hydroxide is essential for formate and carbonate formation. The rapid formation of water as a consequence of the Guerbet reaction in our standard isobutanol forming system using sodium methoxide as the base therefore results in the same products being formed, even in an initially hydroxide free system.

Reduction of the sodium hydroxide base loading to 150 mol% with pre-catalyst 1 maintains the activity (entry 4) but reducing the base loading further has a detrimental impact;

§ After cooling the autoclave to room temperature, the residual pressure, when using pre-catalyst 3 and NaOH base, is 22 bar whereas with pre-catalyst 1 it is 8 bar. This indicates higher formate/carbonate formation with pre-catalyst 3.

¶ On removing the volatiles from the post-reaction mixture, small amounts of formate and carbonate were observed by NMR spectroscopy, presumably due to trace amounts of water from the solvent.

for example, a reduction in sodium hydroxide loading to 50 mol% resulted in an isobutanol yield of only 11% at 68% selectivity over other liquid products (entry 6). It has previously been proposed that stoichiometric alkoxide base loadings are needed due to base degradation over time by the water produced, forming catalytically-inactive hydroxide.^{10b} Clearly, this cannot be the case when using catalyst 1 since sodium hydroxide is still an effective base. However, we do observe the further reaction of sodium hydroxide to sodium carbonate during catalysis, via sodium formate. Crucially, neither sodium formate nor carbonate are effective bases in our system (Table 1, entries 7 and 8), a major issue being their insolubility in the reaction mixture as well as their lower pK_a. So, a high concentration of sodium methoxide (or hydroxide) is required at the beginning of each reaction to ensure that appreciable amounts of active alkoxide (or hydroxide) remain during the reaction before it is degraded to inactive carbonate.

Water tolerance investigations

The water tolerance of catalysts 1 and 2 was examined. We have previously reported that catalyst 1 is tolerant to the addition of low levels of water (0.62 mL, 2 equivalents relative to ethanol) at the beginning of the reaction (Table 1, entry 3).⁹ Addition of water in the same way when using catalyst 2 had a more detrimental effect on the activity and selectivity for isobutanol formation (Table 1, compare entries 10 and 11). This was perhaps surprising given the better performance of in situ formed pre-catalyst [RuCl₂][Jr⁶-p-cymene)]₂/(diphenylphosphino) ethyl-amine over [RuCl₂][Jr⁶-p-cymene)]₂/ dpdm in ethanol homocoupling to n-butanol in the presence of water.^{6c} As the water concentration was increased to a level similar to that found in fermentation broths, a decrease in both isobutanol yield and selectivity was observed with catalyst 1 (Fig. 2, Table S1†), but acceptable yields and selec-

tivities were still achieved. For example, with the addition of 5 mL of water to the system (equivalent to a molar methanol : ethanol : water ratio of 14.4 : 1 : 16.2), an iso-butanol yield of 36% at high selectivity (78%) was obtained. This level of water is typical of a fermentation broth, the ethanol content of which may be as high as 15 wt% from corn starch feedstocks.^{13a}

The addition of water to the system will lower the concentration of the base. As we have shown that a lower initial base loading results in a loss of activity, the same trend is expected on addition of water. Burk et al.^{14b} also observed this effect, noticing that in lowering the initial alkoxide concentration in the heterogeneous rhodium-catalysed conversion of n-butanol to 2-ethyl-1-hexanol, the rate of product formation significantly decreased. A reaction was also carried out using catalyst 1 with air-saturated solvents and 5 mL of water (Table S1†). Although a further drop in activity was observed compared to a nitrogen saturated system, a good isobutanol yield (27%) and selectivity (82%) were still achieved.

Analysis of the solid side-products

Solid side-products are often ignored in this area of catalysis, with selectivity being defined as selectivity within the liquid fraction. Clearly, as well as giving misleadingly high figures of merit, this ignores products that can give insight into competing reaction mechanisms. Analysis of the solid side-products formed in our system confirmed them to comprise predominantly of sodium formate, carbonate and hydroxide, with small amounts of sodium acetate and methoxide formed (Table 2; ESI† Table S4). The production of significant amounts of sodium hydroxide when using sodium methoxide as the base (entry 1) is consistent with the high levels of water produced in the Guerbet reaction, converting the methoxide base to hydroxide. A comparison of entries 1 and 2 shows that a similar composition of solids is produced on the use of either sodium hydroxide or methoxide base. With increased addition of water to the system, there is a

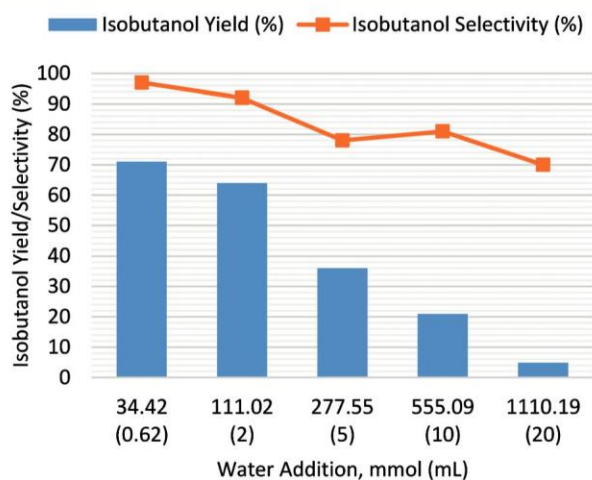


Fig. 2 Effect of water on isobutanol yield and selectivity using catalyst 1. Conditions: 1 mL (17.13 mmol) ethanol, 10 mL (247.13 mmol) methanol, 0.1 mol% 1, 200 mol% NaOH (mol% based on the ethanol substrate), water as stated, 180 °C, 2 h.

Table 2 Analysis of the solids obtained from the post-reaction mixture

Entry ^a	Water (mL)	Composition of solid ^d (wt%)		
		Sodium hydroxide	Sodium formate ^b	Sodium carbonate ^c
1 ^e	—	37	19	37
2	—	49	12	35
3	0.62	43	10	39
4	5	57	9	33
5	20	60	15	23

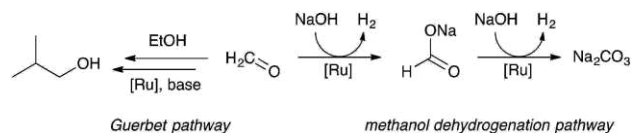
^a Conditions: 1 mL (17.13 mmol) ethanol, 10 mL (247.13 mmol) methanol, 0.1 mol% 1, 200 mol% NaOH (mol% based on the ethanol substrate), water as stated, 180 °C, 2 h. ^b Amount of sodium formate formed calculated by NMR spectroscopy using DMSO as standard. ^c Amount of sodium carbonate formed calculated from microanalysis for inorganic carbon. ^d Other solid products are sodium acetate and methoxide (see the ESI, Table S4), with the remaining solid presumed to be sodium hydroxide. ^e 200 mol% NaOMe.

reduction in sodium formate and carbonate formation. This is consistent with the lower residual hydrogen pressure in the autoclave observed with increased addition of water. For example, entry 2 produced a residual pressure of 8 bar, whilst entry 5 resulted in a residual pressure of 5 bar. This trend in reduction of side-product formation with increased addition of water follows that of isobutanol formation, demonstrating the decrease in catalyst activity with increasing water addition.

Catalyst stability, role of the base and mechanism

In order to investigate the stability of the transition metal complex to water, pre-catalyst 1 was heated in an ethanol/ methanol mixture without base under our standard conditions. This led to the conversion of 1 into two major species identified as trans-[RuH(JCO)(Jdppm)₂]Cl (4) and trans-[RuCl(JCO)(Jdppm)₂]Cl (5) (see the ESI,† section 5.1).²⁰ These carbonyl complexes are presumably formed by decarbonylation reactions of ethanol or methanol.^{7d,21} No Guerbet products were formed confirming the need for basic conditions and suggesting that the carbonyl species poison the catalysis unless a base is present to remove the carbonyl ligand. Milstein et al. have reported the formation of an off-cycle carbonyl species, [RuH(JCO)₂(JPNPⁱPr)], incorporating a de-aromatised P–N–P pincer ligand, which can be converted to a coordinatively unsaturated active ethanol to n-butanol catalyst by the loss of CO under basic conditions.^{7d} Likewise, Szymczak et al. proposed that the deactivated catalyst in their ethanol to n-butanol system takes the form of a ruthenium-carbonyl species.^{7e} Carrying out the same reaction but with addition of 0.62 mL of water also resulted in the formation of 4 and 5 as well as increased amounts of an unidentified cis-diphosphine complex. The similarity in these experiments implies that water does not have a detrimental impact on the pre-catalyst, at least in the absence of base. This stability is perhaps not surprising given that the synthesis of pre-catalyst 1 is carried out under aqueous conditions.²² A second experiment in which pre-catalyst 1 was heated in methanol with sodium hydroxide (ethanol omitted to prevent Guerbet coupling) revealed that carbonyl complexes 4 and 5 were not detected (see the ESI,† section 4.1). This suggests that base depletion via the mechanisms outlined previously can have the added detrimental effect of leading to the deactivation of the transition metal species into these inactive carbonyl complexes. The same major transition metal species, observed by ³¹P{¹H} NMR spectroscopy, were formed with or without the addition of water to the basic system (see the ESI,† section 5.3). The three major peaks (16.5, 22.1 and 35.7 ppm) are also observed in the ³¹P{¹H} NMR spectrum of the post-reaction mixture of a standard isobutanol forming reaction (see the ESI,† Fig. S8). We have previously reported that ruthenium-hydride complexes are the likely catalytic resting species in our systems.⁶

Scheme 2 illustrates the proposed alternative reaction pathways that the formaldehyde generated can follow; either Guerbet condensation or a methanol dehydrogenation path-



Scheme 2 Proposed reaction pathways for formaldehyde generated during catalysis

way, which results in the formation of sodium formate and carbonate. The consumption of base into Guerbet-inactive sodium formate and carbonate bases eventually leads to the deactivation of the system. Detailed mechanistic studies of methanol dehydrogenation involving catalyst 3 and its derivatives have been carried out elsewhere.^{19,23} Presumably, similar routes may be operating with 1 and mechanistic studies are currently underway to further examine these competing processes along with the Guerbet mechanism. Examination of the proposed mechanism highlights the importance of the base in the activation of the ruthenium catalyst, in mediating the aldol condensation and in regenerating off-cycle ruthenium carbonyl species.

Towards fermentation broths

Commercial alcoholic drinks provide a useful surrogate for ethanolic fermentation broths, which are essentially produced in the same way and contain both water and other impurities such as unfermented sugars. The tolerance of catalyst 1 to a variety of ethanol sources was tested (Table 3). The ethanol content (ABV) varied from 45% to 5%, but in each case the same amount of ethanol (17.13 mmol) was added to the reaction in place of pure ethanol. Remarkably, catalyst 1 was tolerant to the use of these ethanol sources; the trend in terms of both yield and selectivity simply follows the water content (see the ESI,† Fig. S1 and Table S2). This has

Table 3 Using alcoholic drinks as the ethanol source

Entry ^a	Ethanol source (ABV) ^b	Ethanol conversion ^c (%)	Yield (selectivity) ^d	
			Isobutanol	Other
1	Raki (45)	79	72 (93)	7.1 (7.2)
2	Gin (41.2)	71	64 (91)	6.9 (8.8)
3	Brandy (36)	67	61 (91)	6.4 (9.0)
4	Port (20)	51	44 (87)	6.9 (13)
5	Sherry (17.5)	48	41 (86)	7.2 (14)
6	White wine (13.5)	45	39 (88)	5.9 (12)
7	Red wine (13.5)	47	40 (86)	6.8 (14)
8	Lager (8.5)	35	29 (85)	5.9 (16)
9	Ale (5)	14	9.9 (74)	4.1 (26)

^a Conditions: ethanol source (17.13 mmol), 10 mL (247.13 mmol) methanol, 0.1 mol% 1, 200 mol% NaOH (mol% based on the ethanol substrate), 180 °C, 2 h. ^b See the ESI general experimental information for further details of the alcoholic drinks used in this study. ^c Conversion of ethanol based on the total amount of liquid Guerbet products obtained as determined by GC analysis. ^d Total yield and selectivity of Guerbet products in the liquid fraction as determined by GC analysis.

significant implications in that the other components such as sugars and sulfites appear to have little effect on the catalytic activity.

Xu and Mu et al. have reported that ferulic acid, a common biogenic component in a fermentation broth derived from inulin, is detrimental to isobutanol formation using a heterogeneous iridium catalyst, decreasing ethanol conversion by 60%.^{10d,24} In contrast, addition of trans-ferulic acid to our system did not cause any loss of catalyst activity (see the ESI,† Table S1).

Conclusions

The pre-catalyst trans-[RuCl₂(Jdppm)₂] (1) was found to be unique amongst the catalysts screened due to its ability to transform aqueous ethanol/methanol mixtures to isobutanol in good yield and excellent selectivity. Key to this catalyst's success is both its tolerance to water and its ability to utilise a hydroxide rather than an alkoxide base. Catalysts 2 and 3 incorporating P–N and P–N–P ligands, respectively, lose both yield and selectivity under the same conditions, a major problem being the promotion of competing side reactions resulting in the formation of inactive formate and carbonate salts. The tolerance of our system to both water and other biogenic impurities is a step forward in converting a crude fermentation broth to an advanced biofuel, significantly lowering the total cost of biofuel production.

Experimental

Materials

Complexes 1 (ref. 22) and 2 (ref. 25) were prepared according to literature procedures. Catalyst 3 was purchased from Sigma-Aldrich and used as received. All reagents were purchased from commercial suppliers and used without further purification unless otherwise stated in the ESI.† Full experimental details can be found in the ESI.†

Typical procedure for the Guerbet coupling of ethanol/ methanol to isobutanol and product analysis: taking Table 1, entry 2 as an example (mol% relative to the ethanol substrate): trans-[RuCl₂(Jdppm)₂] (1) (0.016 g, 0.017 mmol, 0.1 mol%) and NaOH (1.37 g, 34.26 mmol, 200 mol%) were added to a clean, oven dried PTFE sleeve equipped with a stirrer bar in air. The PTFE sleeve was then sealed within the autoclave which was evacuated and re-filled with nitrogen three times. Methanol (10 mL, 247.13 mmol) and ethanol (1 mL, 17.13 mmol) were injected into the autoclave through an inlet against a flow of nitrogen. The autoclave was sealed and placed in a pre-heated (180 °C) aluminium heating mantle for 2 h. After 2 h, the autoclave was cooled in an ice-water bath. Once at room temperature, any residual pressure was released from the autoclave. A portion of the solution was then passed through a 1 cm plug of acidic aluminium oxide and analysed by GC-FID (100 µL sample, 25 µL n-pentanol standard, 1 mL of methanol).

The above procedure was modified to add degassed water along with the ethanol and methanol substrates or to replace analytically pure ethanol with the desired alcoholic beverage (equivalent to 17.13 mmol ethanol) as required.

Conflicts of interest

There are no conflicts to declare.

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